Synopsis

Nanoparticles exhibit novel physical properties originating from electron and vibrational confinements and the surface effects In this thesis, we have investigated optical, vibrational and electronic properties of different semiconducting nanoparticles by Optical absorption, Raman and X ray photoemission spectroscopic techniques We have also presented the finite size effect of the platinum particles on the catalytic properties of the carbon supported Pt electrodes by using X-ray photoemission spectroscopy

Raman scattering is one of the powerful probes to obtain useful informations on the vibrational states Raman scattering from the low dimensional systems has been used to investigate confined optical phonons, surface or interface optical phonons and con fined acoustic phonons On the other hand, since X-ray photoemission spectroscopy is a highly surface sensitive technique, it can be used to examine the purity and the stoichiometry of the surface of the particles under study In **Chapter 1**, we have presented a brief review of these two techniques in order to focus the motivation of the present research work The preparation, characterization of the samples and the experimental techniques involved in this work have been described in **Chapter 2**

In recent times, porous silicon (PS) grown on doped Si wafer by anodic electrochemical etching has attracted considerable interest due to its intense visible photoluminescence (PL) and electroluminescence properties It has been suggested that the effect arises from the quantum confinement of electrons and holes in the nanoscale silicon units formed during electrochemical etching In an alternative model, formation of Si based compounds like SiH_n, siloxene ($Si_6O_3H_6$) and its derivatives and different defect

states at Si/SiO_2 interfaces have been attributed to be the source of luminescence Till today, the origin of visible photoluminescence in PS is very much controversial In **Chapter 3 Part a**, we have discussed the different models in light of our own work on photoemission, Raman and photoluminescence studies of the PS Our experimental results are the following (a) The surface layer of PS is essentially a fluorine admixed SiO_2 phase, while Si O F composition of the subsurface region is 2 1 0 02 With the possibility of the existence of the hydrogen in this composition it appears that beyond highly oxidized surface, PS does contain fluorine substituted siloxene derivative (b) It is known that the optic Raman mode in nanoparticles of Si shifts to lower frequencies and is asymmetric due to phonon confinement If the observed PL in PS is associated with the band to band recombination in the nanoparticles, the blue shift in PL is expected to be correlated with the red shift in the Raman peak position with respect to crystalline silicon We find that in PS there is no correlation between the blue shift in PL band and the red shift in Raman spectrum The clear absence of correlation goes against the confinement model (c) Isochronal thermal annealing studies (annealing temperature varied from room temperature to 900 °C with a step of 50 °C) were carried out to understand the influence of hydrogen desorption from the surface of PS at 350 °C and repassivation by oxygen at higher annealing temperatures Our results indicate that the origin of visible PL in PS can be better explained by a new hybrid model, which incorporates both nanostructured silicon units acting as the reservoir of the electron-hole pairs and siloxene like derivatives and other defects located outside the nanoparticles as radiative luminescent centers

PS has been shown to have fractal morphology below a certain length scale The fracton dimension $\tilde{d}$ characterizes the vibrational density of states, $g(\omega) \sim \omega^{(\tilde{d}-1)}$ of the fractal network These fracton modes can show up in low frequency Raman scattering experiments where the scattered intensity $I(\omega)$ by fracton modes samples the density of states to give $I(\omega) \propto \omega^{\nu-1}[n(\omega)+1]$, where $\nu = [\tilde{d}(2d_\phi + \tilde{D})/\tilde{D}] - 1$ Here $[n(\omega)+1]$ is the usual Bose-Einstein factor and d_ϕ is the geometrical exponent

describing the localization of the fractons in real space **In Chapter 3 Part b**, we have studied the vibrational properties of the fractal structure in PS by low frequency Raman scattering experiments Taking Hausdorff dimension $\bar{D}$ to be 2 5, the value of $\tilde{d}$ obtained is 1 42 which is close to the theoretically predicted value of 4/3

In **Chapter 4**, we have reported the optical and vibrational properties of CdS_xSe_{1-x} (commercially available Schott filter glass - GG495 and OG590) and CdS nanoparticles embedded in silica matrix prepared by using sol gel route Considering the effect of the size distribution of the particles on the absorption spectrum, the average size and the size distribution of the particles in these samples have been estimated by matching calculated optical absorption spectra for such systems with the observed spectra To calculate the theoretical spectrum, we have assumed the log-normal distribution, $P(d)$, of the particle diameter in conjunction with the allowed electronic transition states as obtained from the effective tight binding model These results have been compared with the sizes obtained from the polarized low frequency Raman spectroscopic measurements, where the low frequency Raman peak, associated with the confined acoustic phonons, is inversely proportional to the diameter of the particle (as deduced from Lamb's theory of the elastic vibrations of a sphere) The width of the size-distribution function $P(d)$ is estimated from the fitting of the low frequency Raman and the optical absorption spectra with the convolution of $P(d)$ and the appropriate Lorentzian function A study on the stability of the CdS_xSe_{1-x} particles in the sample GG495 with heat treatment shows that these particles in the glass matrix are stable till 500 °C Further annealing of the sample results in increase of the average particle size The presence of multiphonon Raman modes and surface optical modes in these samples have also been investigated The effect of confinement on the acoustic and optical phonons is studied in CdS nanoparticles embedded in silica matrix

In Chapter 5, we have provided spectroscopic studies on small PbI_2 clusters These clusters of size 12, 18 and 29 Å are prepared in different organic solvents by colloidal

route and characterized by the blue shift in optical absorption spectra We have shown that the blue shifted absorption band from the clusters are not due to the presence of I_3^- ions, as suggested previously, but are characteristic of the clusters itself We have investigated the mechanism of formation and the origin of the stability of the clusters in the solvents Our results suggest that the particular sizes of the microcrystallites formed in a solvent via the colloidal route are entirely determined by the solubility of the bulk PbI_2 in that solvent The photoemission spectra of Pb and I core levels of the clusters establish that the stability of the microcrystallites arises from the presence of excess iodine ions surrounding the clusters The long term stability of these clusters in the solvents has also been investigated

In **Chapter 6**, we present vibrational characteristics and microstructures due to variation in the pore morphology of different phases (boehmite, γ-, δ- and α-) of the alumina gel prepared by sol-gel route The high temperature boehmite gel is composed of nanocrystalline platelets with an average size of $\sim$ 60 Å and a narrow size distribution The gel is highly porous (porosity $\sim$ 60-70 %) The dehydration of the boehmite to other phases represents topotactic deformation of the network and is accompanied by changes in the morphology of the porosity The different phases are characterized by powder X-ray diffraction method The main Raman line in the boehmite phase is red shifted as well as asymmetrically broadened with respect to that of the crystalline boehmite, signifying the nanocrystalline nature of the gel Our low frequency Raman data suggest that the pore morphology in the boehmite alumina gel can be best characterized in terms of fractals below a length scale $\sim$ 70 Å Taking Hausdorff dimension $\tilde{D}$ of the boehmite gel to be 2 5, the value of fracton dimension is calculated to be 1 33

It is imperative to employ platinum-metal based catalysts in Direct Methanol-Air Fuel Cell electrodes Since the size of the platinum particles in platinized carbon catalysts affect their catalytic activity, we have performed X ray photoemission spectroscopic measurements to quantify the concentration of Pt, PtO and PtO_2 in these

samples and the results have been discussed in **Chapter 7** The study reveals that the oxidic contents of platinized carbon samples with smaller Pt particles is higher in comparison to that in the samples with larger Pt particles The role of surface functional groups in these samples towards their catalytic nature is also discussed